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By H. C. Ko and R. R. Brown

UNITED STATES DEPARTMENT OF THE INTERIOR

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ENTHALPIES OF FORMATION OF $ZnO{\cdot}2ZnSO_4$ AND $CoSO_4{\cdot}6H_2O$

By H. C. Ko[1] and R. R. Brown[1]

ABSTRACT

As part of the Bureau of Mines effort to provide thermodynamic data for the advancement of mineral technology, the standard enthalpies of formation for $ZnO{\cdot}2ZnSO_4$ and $CoSO_4{\cdot}6H_2O$ were determined by HCl acid solution calorimetry. The values are -550.31 ±0.28 and -641.33 ±0.15 kcal/mol, respectively.

INTRODUCTION

Zinc oxysulfate ($ZnO{\cdot}2ZnSO_4$) is known as an intermediate compound in the decomposition process of zinc sulfate ($ZnSO_4$). Cobalt sulfate hexahydrate ($CoSO_4{\cdot}6H_2O$) is the product of the sulfatizing and leaching of cobalt ores. Both zinc and cobalt are important critical metals. Zinc is used largely in corrosion protection and in diecasting, and cobalt is used in high-temperature alloys and powder compacts.

There are two values reported in the literature (5, 10)[2] for the enthalpy of formation of $ZnO{\cdot}2ZnSO_4$ that are in good agreement. However, a third value (8) is in disagreement with the two by about 14 kcal/mol. For the enthalpy of formation of $CoSO_4{\cdot}6H_2O$, two values reported in the literature (4, 11) are in good agreement. However, one of these was derived from heat-of-solution measurements on compounds where the number of hydrates was not of exact stoichiometry (4), and the other (11) could have an uncertainty of 2 kcal/mol. For these reasons, the objective of this investigation was to establish more accurately the standard enthalpies of formation of these two compounds by HCl solution calorimetry, as part of the Bureau of Mines effort to provide basic thermodynamic data for advancement of mineral technology and energy conservation.

MATERIALS

Zinc oxysulfate: $ZnO{\cdot}2ZnSO_4$ was supplied by Stanford Research Institute. It was prepared by heating anhydrous zinc sulfate at 700-735° C in air for 2 weeks. The sample was then transferred to a Pyrex[3] container and held at 325° C under

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[3]Reference to specific brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

vacuum for 15 hours. Chemical analysis indicated 60.37 pct ZnO, and thermogravimetric analysis indicated a weight loss corresponding to 39.58 pct as SO_3. These values were in excellent agreement with the theoretical values of 60.39 pct ZnO and 39.61 pct SO_3 for $ZnO \cdot 2ZnSO_4$. Spectrographic analysis showed metallic impurities of Cu, Mg, and Si that totaled less than 40 ppm. The X-ray diffraction pattern was in agreement with the published powder diffraction pattern for $ZnO \cdot 2ZnSO_4$ [PDF Card 16-821 (6)].

Zinc oxide: Ultrapure ZnO (Alfa Products, Ventron Division, 99.999 pct) was dried at 425° C for 4 hours. Weight loss was negligible. X-ray diffraction analysis indicated only ZnO present. Spectrographic analysis detected no metallic impurities.

Cobalt sulfate hexahydrate: $CoSO_4 \cdot 6H_2O$ was obtained from Spex Industries, Inc. Spectrographic analysis showed that total metallic impurities were less than 60 ppm. X-ray diffraction pattern matched that given in powder diffraction file [PDF Card 16-304 (6)]. Chemical analysis showed 22.30 pct Co and 36.80 pct SO_4, compared with theoretical values of 22.40 and 36.51 pct, respectively.

Cobalt oxide (CoO): High-purity cobalt metal (fine powder, 99.999 pct, from Aldrich Chemical Co.) was initially oxidized in a platinum boat in a muffle furnace by heating at 1,000° C in air. The sample was ground and reheated for two 1-hour heating periods with essentially no additional weight gain. X-ray analysis of the product indicated a mixture of CoO and Co_3O_4. This material was ground and given a final heating in oxygen in a tube furnace at 1,100° C for 2 hours. After the furnace was cooled to 1,000° C, the oxygen was replaced with high-purity argon. The Vycor tube containing the platinum boat was removed from the furnace, and the sample was then allowed to cool rapidly under a flow of argon. This procedure prohibited the reoxidation of the CoO to Co_3O_4 during cooling. X-ray analysis of the product indicated only CoO, matching PDF Card 9-402 (6). Spectrographic analysis showed only metallic impurities of Sn, Si, and Ni, totaling less than 300 ppm.

Acids: Sulfuric acid of the composition (H_2SO_4+$6H_2O$) was used as one of the solutes in the heat-of-solution experiments. Hydrochloric acid, 4.360 molal or (HCl+$12.731H_2O$), was used as the solvent in all of the experiments. These acids were made from reagent-grade materials, and analyses confirmed the compositions as given.

APPARATUS AND PROCEDURE

The apparatus used for determining enthalpy of formation was an isoperibol solution calorimeter. The apparatus and procedure are described elsewhere (7). The operating temperature was 298.15 K.

RESULTS

The reaction schemes for determining the enthalpies of formation of $ZnO \cdot 2ZnSO_4$ and $CoSO_4 \cdot 6H_2O$ are given in tables 1-2. The symbols c, ℓ, and sol denote substances that are crystalline, liquid, and in solution, respectively. The reactions are written to show that the appropriate stoichiometry is maintained. Approximately 0.0025 mol of $ZnO \cdot 2ZnSO_4$ and 0.0134 mol of $CoSO_4 \cdot 6H_2O$ were used as the weight basis for each reaction scheme, and other substances conformed stoichiometrically with these quantities. The average measured heat values and uncertainties for the individual reactions are also listed in tables 1-2.

TABLE 1. - Calorimetric reaction scheme for $ZnO \cdot 2ZnSO_4(c)$ at 298.15 K

Reaction	ΔH, kcal	Uncertainty, kcal
(1) $2(H_2SO_4+6H_2O)(\ell) = 4H^+(sol) + 2SO_4^{2-}(sol) + 12H_2O(sol)$.....	-2.484	0.014
(2) $3ZnO(c) + 6H^+(sol) = 3Zn^{2+}(sol) + 3H_2O(sol)$.....	-47.613	.030
(3) $14H_2O(\ell) = 14H_2O(sol)$.....	-1.074	.014
(4) $ZnO \cdot 2ZnSO_4(c) + 2H^+(sol) = 3Zn^{2+}(sol) + 2SO_4^{2-}(sol) + H_2O(sol)$	-31.415	.020
(5) $3ZnO(c) + 2(H_2SO_4+6H_2O)(\ell) = ZnO \cdot 2ZnSO_4(c) + 14H_2O(\ell)$		
$\Delta H_5 = \Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4$		
$= -17.608 \pm 0.041$ kcal		

TABLE 2. - Calorimetric reaction scheme for $CoSO_4 \cdot 6H_2O(c)$ at 298.15 K

Reaction	ΔH, kcal	Uncertainty, kcal
(6) $(H_2SO_4+6H_2O)(\ell) = 2H^+(sol) + SO_4^{2-}(sol) + 6H_2O(sol)$.....	-1.242	0.007
(7) $CoO(c) + 2H^+(sol) = Co^{2+}(sol) + H_2O(sol)$.....	-25.217	.022
(8) $H_2O(\ell) = H_2O(sol)$.....	-.0767	.001
(9) $CoSO_4 \cdot 6H_2O(c) = Co^{2+}(sol) + SO_4^{2-}(sol) + 6H_2O(sol)$.....	7.586	.013
(10) $CoO(c) + (H_2SO_4+6H_2O)(\ell) = CoSO_4 \cdot 6H_2O(c) + H_2O(\ell)$		
$\Delta H_{10} = \Delta H_6 + \Delta H_7 - \Delta H_8 - \Delta H_9$		
$= -33.968 \pm 0.027$ kcal		

The assignment of uncertainties was based on the following criteria described by Rossini (9): (1) When several individual values of heat were measured for a reaction, the uncertainty was taken as twice the standard deviation of the mean; (2) when the heats of two or more reactions were combined, the uncertainty was the square root of the sum of the squares of the individual uncertainties.

Reactions 1 and 2 were measured consecutively in 2,260 grams of solvent and reactions 3 and 4 in a fresh batch of 2,260 grams of solvent. Reactions 1 and 3 were studied previously (7) and the corresponding heats of solution of $(H_2SO_4+6H_2O)$ and H_2O are adopted as -1.242 ± 0.007 and -0.0767 ± 0.0010 kcal/mol, respectively. Experimental values of heats of solution for reactions 2 and 4 are listed in table 3 with the mean values and uncertainties. Reactions 1-4 and their heats of reaction, ΔH, can be combined to give the overall reaction 5 and a value of -17.608 ± 0.041 kcal for ΔH_5 at 298.15 K.

Reactions 6-9 were investigated in the same manner as described for reactions 1-4. Reaction 6 is identical to reaction 1, and reaction 8 to reaction 3, except on a molar basis. Experimental heat values for reactions 7 and 9 are also included in table 3 with their mean values and uncertainties. Reactions 6-9 and their heats of reaction can be combined to give the overall calorimetric reaction 10 and a value of -33.968 ± 0.027 kcal for ΔH_{10} at 298.15 K.

TABLE 3. - Experimental heats of solution at 298.15 K, kilocalories per mol

	$ZnO(c)$, reaction 2	$ZnO \cdot 2ZnSO_4(c)$, reaction 4	$CoO(c)$, reaction 7	$CoSO_4 \cdot 6H_2O(c)$, reaction 9
Experimental values.....	-15.890	-31.383	-25.235	7.595
	-15.856	-31.451	-25.254	7.578
	-15.857	-31.433	-25.197	7.576
	-15.876	-31.447	-25.193	7.606
	-15.878	-31.392	-25.198	7.583
	-15.865	-31.379	-25.285	7.617
	-15.875	-31.424	-25.234	7.566
	ND	-31.412	-25.208	7.565
	ND	ND	-25.195	ND
	ND	ND	-25.169	ND
Mean.....	-15.871	-31.415	-25.217	7.586
Uncertainty....	±.010	±.020	±.022	±.013

ND Not determined.

Combination of the overall reaction 5 and ΔH_5 with enthalpies of formation of $ZnO(c)$, $(H_2SO_4+6H_2O)(\ell)$, and $H_2O(\ell)$, given by reactions 11, 13, and 14 and shown in table 4, yields the value for the standard enthalpy of formation, $\Delta Hf^\circ_{298.15}$, of $ZnO \cdot 2ZnSO_4$ as represented by reaction 15 in table 4. Similarly, combination of reaction 10 with the enthalpy of formation of $CoO(c)$, reaction 12, reactions 13 and 14, shown in table 4, yields $\Delta Hf^\circ_{298.15}$ of $CoSO_4 \cdot 6H_2O(c)$ as represented by reaction 16. The symbol g denotes substances that are gaseous, and rh denotes the rhombic form of crystalline sulfur.

TABLE 4. - Derivation of enthalpies of formation of $ZnO \cdot 2ZnSO_4(c)$ and $CoSO_4 \cdot 6H_2O(c)$ at 298.15 K

Reaction	ΔH, kcal	Uncertainty, kcal	Reference
(5) $3ZnO(c) + 2(H_2SO_4+6H_2O)(\ell) = ZnO \cdot 2ZnSO_4(c) + 14H_2O(\ell)$	-17.608	0.041	This work.
(10) $CoO(c) + (H_2SO_4+6H_2O)(\ell) = CoSO_4 \cdot 6H_2O(c) + H_2O(\ell)$...	-33.968	.027	Do.
(11) $Zn(c) + 1/2O_2(g) = ZnO(c)$.....	-83.762	.065	2
(12) $Co(c) + 1/2O_2(g) = CoO(c)$.....	-56.76	.10	3
(13) $H_2(g) + S(rh) + 2O_2(g) + 6H_2O(\ell) = (H_2SO_4+6H_2O)(\ell)$..	-209.024	.100	2, 10
(14) $H_2(g) + 1/2O_2(g) = H_2O(\ell)$.....	-68.315	.010	10

(15) $3Zn(c) + 2S(rh) + 9/2O_2(g) = ZnO \cdot 2ZnSO_4(c)$

$\Delta Hf^\circ[ZnO \cdot 2ZnSO_4(c), 298.15\ K] = \Delta H_{15} = \Delta H_5 + 3\Delta H_{11} + 2\Delta H_{13} - 2\Delta H_{14}$
$= -550.31 \pm 0.28$ kcal/mol

(16) $Co(c) + S(rh) + 6H_2(g) + 5O_2(g) = CoSO_4 \cdot 6H_2O(c)$

$\Delta Hf^\circ[CoSO_4 \cdot 6H_2O(c), 298.15\ K] = \Delta H_{16} = \Delta H_{10} + \Delta H_{12} + \Delta H_{13} + 5\Delta H_{14}$
$= -641.33 \pm 0.15$ kcal/mol

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DISCUSSION

There are a few values reported for the enthalpy of formation of $ZnO \cdot 2ZnSO_4$. Ingraham and Kellogg (5) studied the decomposition of $ZnSO_4$ and $ZnO \cdot 2ZnSO_4$ in a closed system. They reported a value of -551.10 ±1.0 kcal/mol for $\Delta Hf^\circ_{298.15}$ of $ZnO \cdot 2ZnSO_4$. Wagman and others (10) reported a value of -551.3 kcal/mol. Our value of -550.31 kcal/mol is in good agreement with these two values. Komlev and Philipchuk (8) studied the Zn-S-O system and determined the equilibrium constants by a static manometric method. They reported -565.5 kcal/mol for ΔHf° of $ZnO \cdot 2ZnSO_4$ at 298.15 K. This value deviates from our value by more than 15 kcal.

Goldberg and others (4) measured heats of solution of $CoSO_4$(c) and several hydrates to calculate $\Delta H^\circ_{298.15}$ of $CoSO_4 \cdot 6H_2O$. Their "hexahydrate" was actually a mixture of $CoSO_4 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$, the actual composition being $CoSO_4 \cdot 6.075H_2O$. Their calculated result for $\Delta H^\circ_{298.15}$ of $CoSO_4$ was -640.8 kcal/mol. Using the more recent values of enthalpy of formation of SO_4^{2-}(aq)(2) and of CoO(c)(3) with Goldberg's data, the $\Delta H^\circ_{298.15}$ was recalculated to be -641.09 kcal/mol. Wagman and others (11), based on the data of Adami and King (1), listed -641.4 kcal/mol, which could have a maximum uncertainty of 2 kcal. Our experimental value of -641.33 ±0.15 kcal/mol is in excellent agreement with these values and establishes this value with considerably smaller uncertainty. In any hydrate, ΔHf° contains the enthalpy of formation of water; for example, in a hexahydrate, ΔHf° contains -409.9 kcal for the formation of 6 mols of water, and this value constitutes a large portion of ΔHf° for the hydrated salt. A high accuracy in the data is especially desirable in the measurement of successive hydration of compounds. For example, the heat of hydration of the hexahydrate to the heptahydrate is -2.49 kcal, which refers to $CoSO_4 \cdot 6H_2O$(c) + $H_2O(\ell) = CoSO_4 \cdot 7H_2O$(c). An uncertainty of 0.1 pct in the value of enthalpy of formation of either hydrate would result in an uncertainty on the order of 30 to 40 pct in the enthalpy of successive hydration.

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